



## Feature Article

# Gold promoted imine production by selective gas phase reductive coupling of nitrobenzene and benzaldehyde



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## ARTICLE INFO

## Article history:

Received 22 September 2016

Received in revised form 7 November 2016

Accepted 29 November 2016

Available online 2 December 2016

## Keywords:

Gas phase reductive coupling

Nitrobenzene

Benzaldehyde

Imine

Supported gold

## ABSTRACT

The feasibility of gas phase continuous reductive coupling of nitrobenzene and benzaldehyde for imine (*N*-benzylideneaniline) synthesis over oxide ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{MgO}$ ) supported Au and Pd (1.0–3.4% w/w) has been demonstrated. Reaction over Au/ $\text{TiO}_2$  (mean size = 3.2 nm) delivered 99% selectivity to the target imine. An equivalent level of selectivity was achieved over all the oxide supported Au catalysts with increasing turnover frequency ( $6 \rightarrow 103 \text{ h}^{-1}$ ) for smaller Au particles (7.7  $\rightarrow$  3.2 nm), where nitrobenzene  $\rightarrow$  aniline was rate determining. Lower TOF over Au/ $\text{Fe}_2\text{O}_3$  is linked to the involvement of surface oxygen vacancies that serve to stabilise the nitro-reactant and lower reactivity. Under the same reaction conditions, Pd/ $\text{TiO}_2$  exhibited greater  $\text{H}_2$  chemisorption capacity and higher activity but lower imine selectivity ( $S = 83\%$ ) due to toluene formation (*via* benzaldehyde hydrogenolysis). Reaction at extended contact times (0.2  $\rightarrow$  0.5 s) over Au/ $\text{TiO}_2$  served to enhance imine yield (to 70%).

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## 1. Introduction

Tandem catalytic coupling processes that combine multiple reactions in one “pot” enhance process efficiency by minimising reaction steps with maximum catalyst utilisation. Tandem coupled systems involving cyclisation [1], cycloaddition [2] and Michael-aldol [3] reactions have drawn on homogeneous catalysis. The requirement for catalyst separation and reuse limits efficiency but this can be circumvented by switching to heterogeneous catalysis. Solid catalysts ( $\beta$ -zeolite [4],  $\text{NaAlO}_2$  [5], Rh/Zr- $\beta$ -zeolite [6] and Pd/MgO [7]) have been used in pressurised (up to 5 bar) batch liquid phase tandem reactions for the synthesis of ethers, glycidol, alkylcyclohexanols and nabumetone. Continuous gas phase operation has clear benefits in terms of reduced downtime and higher throughput but there has been limited work on catalytic tandem reactions [8–10]. We can flag butanol synthesis (13% yield) *via* a tandem gas phase hydroformylation-hydrogenation of propene and synthesis gas over a  $\text{SiO}_2$  supported Ru complex (Shvo catalyst) and supported Rh [8] and ethylene dimerization-isomerization to 2-butene over supported Ni [10].

Imines, widely used as organic intermediates in the manufacture of fine chemicals, pharmaceuticals and agrochemicals [11], are typically prepared in multi-step processes starting with amine

synthesis from the corresponding nitro-reactant [12]. Dehydrogenative condensation of alcohols with amines to give imines has been established in liquid phase [13–17] with promising results using supported Au [18,19]. Selectivities up to 99% have been reported in batch imine synthesis using Au on hydroxyapatite [18] and  $\text{TiO}_2$  [19] in coupled reaction of alcohols (benzyl alcohol, cinnamyl alcohol and 1-phenylethanol) with aniline, 1-hexylamine and benzylamine. Oxidative condensation of benzylamines has been studied in liquid phase operation ( $T = 373 \text{ K}$ ,  $P_{\text{O}_2} = 5 \text{ bar}$ ) with exclusivity to imines over ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , carbon and graphite) supported Au [20,21]. The conventional stepwise process (nitro  $\rightarrow$  amine  $\rightarrow$  imine) necessitates multiple reactor operation. Use of nitro-compounds as feedstock in the coupled system can increase efficiency by incorporating the nitro  $\rightarrow$  amine reduction step (Fig. 1, step (I)) within the process. Application of supported Au catalysts in one-pot reductive coupling has not been examined in detail and we could not find any report of nitroarene-aldehyde gas phase conversion. Santos et al. [22] demonstrated one-step synthesis of imine from substituted (vinyl and brominated) nitrobenzene and aromatic aldehydes (benzaldehyde and cinnamaldehyde) over Au/ $\text{TiO}_2$  in batch liquid phase ( $T = 393 \text{ K}$ ,  $P_{\text{H}_2} = 4\text{--}12 \text{ bar}$ ). Here we evaluate the viability of imine production by gas phase continuous reductive coupling of nitrobenzene and benzaldehyde (as model reactants) over Au. As illustrated in Fig. 1, nitrobenzene reduction determines imine production by supplying aniline for condensation. In prior work, we have shown that Au particle size and support redox character play crucial roles in determining catalytic activ-

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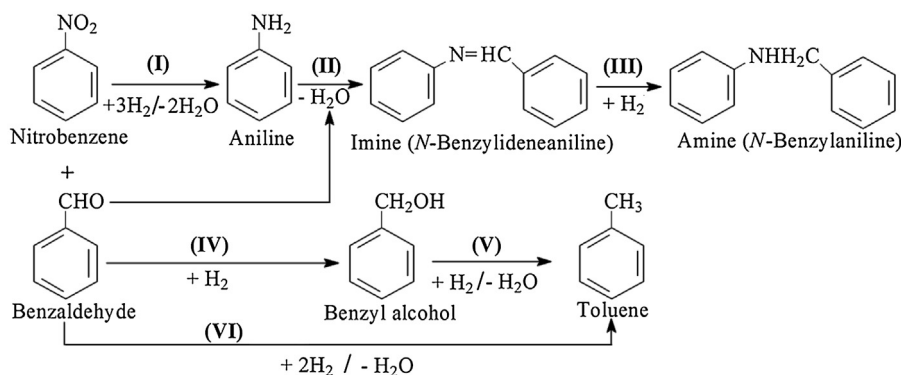


Fig. 1. Reaction scheme for the reductive coupling of nitrobenzene with benzaldehyde.

ity in  $-\text{NO}_2$  reduction [23]. Moreover, control over contact time in continuous operation can govern conversion and reaction rate in selective hydrogenation [24] where increased residence time resulted in elevated conversion in benzonitrile  $\rightarrow$  benzylamine [25] and furfural  $\rightarrow$  2-methylfuran [26]. In this study, we consider these factors and examine the performance of Au on a series of oxides ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{MgO}$ ). Supported Pd is used commercially in nitrobenzene hydrogenation [27]. As selective nitroarene adsorption *via* the  $-\text{NO}_2$  function on  $\text{TiO}_2$  and at the metal- $\text{TiO}_2$  interface serves to enhance amine production rate [28], we have adopted Pd/ $\text{TiO}_2$  as a benchmark.

## 2. Experimental

### 2.1. Catalyst preparation and activation

The supports used were commercial ( $\text{TiO}_2$  (P25, Degussa),  $\text{Al}_2\text{O}_3$  (Puralox, Condea Vista) and  $\text{MgO}$  (Sigma-Aldrich)) or synthesised ( $\text{Fe}_2\text{O}_3$  and  $\text{ZrO}_2$ ) following procedures described elsewhere [29,30]. Gold on  $\text{MgO}$  was prepared by impregnation of  $\text{MgO}$  (10 g, Sigma Aldrich, >99%) with aqueous  $\text{HAuCl}_4$  ( $5 \times 10^{-2}$  M, 50  $\text{cm}^3$ , Sigma-Aldrich, 99%). The slurry was heated (at  $2 \text{ K min}^{-1}$ ) to 353 K under vigorous stirring (600 rpm) and maintained in a He purge for 5 h. Gold on  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  was synthesised by deposition-precipitation with urea (Riedel-de Haën, 99%) as basification agent. An aqueous solution of urea (100-fold excess) and  $\text{HAuCl}_4$  ( $3 - 7 \times 10^{-3}$  M, 400  $\text{cm}^3$ ) was added to the support (10–30 g). The suspension was stirred (600 rpm) and heated (at  $2 \text{ K min}^{-1}$ ) to 353 K, where the pH progressively increased to 6–8 after 3–4 h as a result of urea decomposition [31]. The solid obtained was separated by filtration, washed with distilled water and dried in  $45 \text{ cm}^3 \text{ min}^{-1}$  He at 373 K for 5 h. A supported Pd benchmark was prepared by precipitation of  $\text{Pd}(\text{NO}_3)_2$  ( $4 \times 10^{-3}$  M, 300  $\text{cm}^3$ , Sigma-Aldrich, 99%) on  $\text{TiO}_2$  (10 g), adding aqueous  $\text{Na}_2\text{CO}_3$  (2 M, Riedel-de Haën, 99%) dropwise until  $\text{pH} > 10$  [32]. The slurry was heated (at  $2 \text{ K min}^{-1}$ ) to 353 K and maintained for 4 h. The solid was separated by filtration, washed with distilled water and dried under vacuum at 333 K for 12 h. The catalyst precursors were sieved (ATM fine test sieves) to mean particle diameter = 75  $\mu\text{m}$ . Samples were activated in  $60 \text{ cm}^3 \text{ min}^{-1}$   $\text{H}_2$  at  $2 - 5 \text{ K min}^{-1}$  to 423–603 K and passivated at ambient temperature in 1% v/v  $\text{O}_2/\text{He}$  for *ex situ* characterisation.

### 2.2. Catalyst characterisation

Metal content was measured by atomic absorption spectroscopy using a Shimadzu AA-6650 spectrometer with an air-acetylene flame from the diluted extract in aqua regia (25% v/v  $\text{HNO}_3/\text{HCl}$ ). Temperature programmed reduction (TPR) and  $\text{H}_2$  chemisorption were conducted on the commercial CHEM-BET 3000 (Quan-

tachrome Instrument) unit equipped with a thermal conductivity detector (TCD) for continuous monitoring of gas composition and the TPR Win<sup>TM</sup> software for data acquisition/manipulation. Samples were loaded into a U-shaped Pyrex glass cell (3.76 mm i.d.) and heated in  $17 \text{ cm}^3 \text{ min}^{-1}$  (Brooks mass flow controlled) 5% v/v  $\text{H}_2/\text{N}_2$  at  $2 - 5 \text{ K min}^{-1}$  to 423–603 K, which was maintained until the signal returned to baseline. The activated sample was swept with  $65 \text{ cm}^3 \text{ min}^{-1}$   $\text{N}_2$  for 1.5 h, cooled to reaction temperature (413 K) and subjected to  $\text{H}_2$  pulse (10  $\mu\text{l}$ ) titration. In blank tests, there was no measurable  $\text{H}_2$  uptake on the support alone. Oxygen chemisorption post-TPR was employed to determine the extent of support reduction, where samples were reduced as described above, swept with  $65 \text{ cm}^3 \text{ min}^{-1}$  He for 1.5 h, cooled to 413 K with pulse (50  $\mu\text{l}$ )  $\text{O}_2$  titration. It has been demonstrated that Au contribution to total  $\text{O}_2$  adsorbed is negligible [33]. Nitrogen adsorption-desorption isotherms were obtained using the commercial Micromeritics Gemini 2390p system. Prior to analysis, the samples were outgassed at 423 K for 1 h in  $\text{N}_2$ . Total specific surface area (SSA) was obtained using the standard BET method. Metal particle morphology (size and shape) was examined by scanning transmission electron microscopy (STEM, JEOL 2200FS), employing Gatan Digital Micrograph 1.82 for data acquisition/manipulation. Samples for analysis were prepared by dispersion in acetone and deposited on a holey carbon/Cu grid (300 Mesh). The surface area weighted mean metal size ( $d_{\text{STEM}}$ ) was based on a count of at least 300 particles according to

$$d_{\text{STEM}} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

where  $n_i$  is the number of particles of diameter  $d_i$ .

### 2.3. Catalytic procedure

Catalyst testing was carried out at atmospheric pressure and 413 K *in situ* after activation in a continuous flow fixed bed tubular reactor (i.d. = 15 mm). The catalytic reactor has been described elsewhere [29,30,34] but features pertinent to this study are given below. A layer of borosilicate glass beads served as preheating zone where the reactant was vaporised and reached reaction temperature before contacting the catalyst bed. Isothermal conditions ( $\pm 1$  K) were maintained by diluting the catalyst bed with ground glass (75  $\mu\text{m}$ ), which was mixed thoroughly with the catalyst before loading into the reactor. Reaction temperature was continuously monitored by a thermocouple inserted in a thermowell within the catalyst bed. The reactant(s) (benzaldehyde and/or nitrobenzene) was(were) delivered as an ethanolic solution to the reactor *via* a glass/teflon air-tight syringe and teflon

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